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by

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ABSTRACT

The attrition milling process has been employed to synthesize precursor powders of four different lead titanate based ceramics. Both the alkaline earth and rare earth materials are used as major dopants to modify the lead titanate composition. The influence of dopants and powder processing parameters on the surface area, phase composition, sintering and microstructural properties are discussed.

Keywords: modified lead titanate, synthesis, processing, characterization.

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INTRODUCTION

The phenomenon of piezoelectricity is a characteristic of crystalline materials that lack a centre of symmetry in their crystal structure. This non-centrosymmetry in the crystal structure makes them sensitive towards electromechanical fluctuations. When subjected to mechanical stress, these materials develop an electric charge that is linearly proportional to the applied stress. This phenomenon is reversible in nature and is termed the piezoelectric effect. In the reverse situation, these material undergo geometric deformation proportional to the applied electric field. This phenomenon was first discovered in 1880 by J. and P. Curie during their systematic study on the influence of pressure on the electrical response of a variety of single crystal materials. An excellent review of the earlier developments of piezoelectric effects in single crystals is given by Cady (1).

The progress in the development of practical devices based on the piezoelectric effect has been rather slow. This may be attributed to the difficulties in fabricating single crystal materials into a wide variety of sizes and shapes necessary for device applications. The high costs involved in manufacturing single crystal piezoelectric materials also contributed to its slow growth. It was the pioneering work of Gray (2) and Roberts (3) who showed that piezoelectricity can be induced into polycrystalline barium titanate ceramics under the influence of high d.c. fields (a process known as "poling"), that triggered a flurry of research activity in this area. Barium titanate ceramics exhibited high piezoelectric activity and high permitivity. The ease of fabricating polycrystalline ceramics into various shapes and sizes also contributed favourably towards their development for device applications. Today, piezoelectric ceramics are used in a wide

variety of electromechanical devices, e.g. high intensity sonic and ultrasonic sources in sonar projectors, ultrasonic machining and welding, non-destructive ultrasonic imaging, medical diagnostics, electromechanical filters, high voltage generators, ceramic actuators, hydrophones, microphones, micropositioning devices, robotics, etc.

The barium titanate based ceramic piezoelectrics produced initially were poor in quality or performance. Some of the problems included high dielectric and elastic losses, and higher aging rate (deterioration of dielectric properties with time and temperature). These materials were also difficult to produce as their properties were strongly influenced by the processing conditions. These problems led scientists and engineers working in this area to search for new and improved piezoelectric ceramic materials. Although some of the problems with barium titanate could be significantly reduced by doping it with alkaline earths and transition metal oxides, and a number of new piezoelectric ceramics, e.g., lead titanate, lead niobate, etc. were discovered, their properties were still poor for any device applications. In 1954 Jaffe and co-workers (4) discovered piezoelectricity in solid solutions of lead zirconate-lead titanate (PZT). Compared to the barium titanates these ceramics have relatively lower dielectric and elastic losses at high drive levels, improved piezoelectric properties and material reliability. Currently, various chemical modifications of PZT materials are employed in a variety of commercially available electromechanical devices.

Recently, lead titanate has been the focus of much attention for various device applications. Lead titanate is a ferroelectric material having a perovskite structure similar to barium titanate. The main features of the lead titanate ceramics include: 1) an

order of magnitude lower dielectric constant (~200) compared to barium titanates and PZT ceramics, 2) a high Curie point of about 500°C, 3) an almost negligible aging effect on the dielectric constant, and 4) a large difference between the thickness coupling coefficient (K_t) and planar coupling coefficient (K_p). The disadvantages are: 1) poor sinterability due to large anisotropy in the crystal structure (large c/a ratio), 2) inhomogeneities in the microstructure caused by the volatilization of lead oxide at high sintering temperatures, and 3) severe poling conditions required to induce piezoelectricity in this material. However, the advantages outweigh the disadvantages, and this material is considered to be promising for high temperature, high frequency device applications, e.g., transducer elements for high frequency (ultrasonic) non-destructive testing devices, medical diagnostic apparatus, hydrophones, etc. Compared to PZT ceramics, lead titanate based ceramic array transducers can be operated at higher frequencies, thus providing better image resolution. This is due to the fact that these have a very small lateral or planar mode coupling coefficient allowing width-to-thickness ratio of the transducer element to be greater than one ($w/t>1$). The large planar mode coupling factor in PZT restricts the width-to- thickness ratio of the transducer element to be less than one ($w/t<1$) in order to prevent lateral vibrations from affecting the acoustic beam. This restriction makes it difficult for PZT ceramics to be used for high frequency array transducers. Due to this dimensional limitation and subsequent difficulties in machining plates into a large number of small elements, the operating frequency of the commercially available array transducers is limited to the 5MHz region (5-6).

The sinterability of lead titanate has been shown to be improved by doping it with a variety of alkaline-earth and rare-earth oxides (7-13). Sintering temperature can also be reduced by adding transition metal oxides along with tungsten oxide as mineralizer. Furthermore, the addition of MnO increases the

insulation resistance, and improves the sinterability and poling conditions of lead titanate. CANMET's, Ceramic Section, is involved in the research and development of advanced structural and functional ceramics for a variety of applications in collaboration with Canadian industry. The development of new or improved materials for NDT transducers constitutes an important part of our R & D effort. The detection of subsurface microflaws is crucial if advanced structural ceramic components are to be used in many applications such as in high temperature gas turbines and internal combustion engine parts. This would require development of transducer materials that can operate at frequencies of 50-100 MHz. At present no such transducer element is commercially available. Lead titanate based ceramics are considered promising for these applications. A number of lead titanate based compositions are therefore being developed at CANMET. The influence of various processing and sintering conditions on the densification, microstructure, dielectric and piezoelectric properties of these materials is being investigated. This report describes the effect of processing parameters on the particle size, surface area, phase composition, sintering and microstructure of lead titanate based ceramics containing alkaline-earth and rare-earth oxides as major dopants.

MATERIALS AND METHODS

1. Powder Preparation

Powders were prepared from high purity commercial raw materials in the form of oxides or carbonates. Initially they were dry mixed in a rotary tumbler and then subjected to successive stages of mixing, grinding, drying, calcination, regrinding and redrying before being pressed into discs and sintered.

1.1 Attrition milling

Batches of powder weighing 300-400 g were placed in a 1 L attrition mill container which was filled to about 1/2 capacity with high purity zirconia attrition milling medium (spherical, 3 mm diameter). Water was added to cover the surface of the beads along with 0.55% (by weight) of the deflocculent 'Darvan C'. The slurry was attrition milled for 3 1/2 hours.

1.2 Drying

Three different types of drying techniques were employed to remove water from the powders:

(a) Filtration

Attrition milled powders were filtered through a Buchner funnel fitted with Whatman No. 42 filter paper. This method could only be used for insoluble powders.

(b) Spray drying

Slurries obtained from attrition milling were left to sit overnight before being spray dried. Immediately prior to spray drying, they were placed in a mechanical shaker for 1 hour with 1 cm diameter zirconia attrition medium. The spray drier was a Buchi model 190 mini spray drier set to the following operating conditions:

pump control	-	11
aspirator	-	9
heating	-	10.5

Inlet temperature was set to approximately 200°C while the outlet

temperature was 125°C. This method gave 3 powder fractions: material from (i) the collector, (ii) the heavy particle trap, and (iii) scrapings from the walls of the chamber and passages. Each of these fractions made up approximately 72, 15 and 13 percent, respectively, of the material recovered.

(c) Rotary evaporation

The slurries were placed in a 2-L round-bottomed flask and evaporated down to a small volume at room temperature. A calculated amount of isopropanol was added to remove the remaining water azeotropically and the slurry was evaporated to dryness. The recovered material was left to dry overnight in an oven maintained at 116°C.

1.3 Calcination

Powders were calcined in 50-100 g batches in a zirconia crucible covered with platinum foil. The crucibles were placed in a muffle furnace and heated to 800 or 900°C for 2 hours.

1.4 Regrinding

The calcined batches were attrition milled for 2 hours as described previously except that no deflocculent was added. This step was necessary to break up agglomerated particles formed during calcination.

1.5 Redrying

Calcined and reattrition milled powders were dried by filtration or vacuum evaporation. (These 2 methods were preferred over spray drying because they were less time-consuming).

2. PRESSING

The powders were pressed into 19 mm diameter pellets each weighing between 3.5 and 4.0 g. Enough powder to make 2 pellets was mixed with 5% of a 20% aqueous solution (by weight) of the binder polyvinyl alcohol (PVA). The powder was placed in a lubricated (lubricant 2:1 machine oil:kerosene) die and pressed at 207 MPa for 30 seconds in a manual hydraulic press. The pellet was removed, its sides scraped free of lubricant, crushed and reground in a Diamonite mortar. Reground material was divided into 2 portions, each one pressed at 138 MPa for 30 seconds resulting in two 0.75 inch pellets. Care was taken to ensure that the dies and mortar were thoroughly cleaned between each pressing.

3. PVA BURNOUT

Before sintering, PVA and adsorbed moisture were removed by heating the pellets in an oven at 5°C/min to 300°C and holding for 1 hour, followed by raising the temperature by 15°C/min from 300 to 600°C and holding there for 2 hours.

4. SINTERING

The pellets were sintered in a furnace which heated them to 600°C at a rate of 15°C/min and then to their respective sintering temperatures at 5°C/min.

5. LAPPING AND POLISHING

Sintered pellets were parallel lapped with 600 grit silicon

carbide to ensure the two faces were parallel. Polishing with 2/0 and 3/0 SiC sand paper on a rotary polisher gave a smooth surface for electroding.

6. ELECTRODING

Silver electrode paint (Dupont #4731) was applied to each face, the pellet was allowed to dry and then heated at 15°C/min to 660°C and held for 15 minutes. The pellets were allowed to cool to room temperature and a second coat applied by repeating the aforementioned process.

RESULTS AND DISCUSSION

Compositions of powders

The following is a list of the intended elemental composition of the powders:

Powder	Composition
D1	$Pb_{.765}Ca_{.24}(Fe_{.03}W_{.03}Mn_{.015}Ti_{.97})O_3$
D2	$Pb_{.88}Na_{.24}(Co_{.02}W_{.02}Mn_{.02}Ti_{.97})O_3$
D3	$Pb_{.95}Na_{.1}(Co_{.02}W_{.02}Mn_{.02}Ti_{.97})O_3$
D4	$Pb_{.80}Ce_{.1}(Co_{.02}W_{.02}Mn_{.02}Ti_{.97})O_3$

Surface Area Measurements (BET Method)

Surface areas of the powders in this study were influenced by three different parameters including: 1) powder drying method, 2) calcination temperature, and 3) re-attrition milling of the calcined powders (see Table 1).

The surface area of the powder in at least one case was related to the sintered density of the final product. Pellets of D1 calcined at 900°C would not give sintered densities better than 86% theoretical density. When re-attrition milled (see "after regrinding" column of Table 2), pellets of the same powder under the same conditions attained densities of 93% theoretical or better. As a result of this, powders calcined at 900°C or higher were subsequently re-attrition milled after calcination.

Of the 3 drying methods described, filtration appeared to give the highest surface area. Spray drying produced soft agglomerates of slightly better surface area than vacuum evaporation.

X-Ray Powder Diffraction Data

Powder diffraction patterns of oxides and carbonates that were mixed and attrition milled together showed a $PbTiO_3$ (perovskite) structure after calcination around 800-900°C. Only in some cases trace amounts of unreacted oxides/carbonates or other unidentified phases were detected at these temperatures. A typical XRD pattern is shown in Fig. 1. The diffraction patterns clearly showed the effect of dopants on d-spacings in the material. Unit cell volumes and tetragonality (c/a) were calculated by indexing the diffraction patterns and obtaining "a" and "c" values using a lattice parameter calculations program developed at CANMET. Theoretical density calculations were useful in determining optimum sintering conditions. The theoretical density was calculated by dividing the overall formula weight of the powder by Avagadro's number and the unit cell volume. Densities were calculated from the masses and dimensions of lapped, polished pellets. Densities measured by Archimedes method were 2-3% larger than calculated values. The former procedure was followed because the buoyancy method is not recommended for objects weighing less than 50 g (ASTM C373-72).

Data from the XRD studies, optimum sintering temperatures and observed densities for the above compositions are summarised in Table. 2. The cell tetragonality and theoretical density of undoped lead titanate is also given for ready reference. All sintered materials had densities that were 92% theoretical or better. The optimum sintering temperatures and densities of the materials appear to be influenced by the sample composition. Sample D4 exhibited the highest sinter densities. The high soda content may be responsible for observed low sintering temperatures for D2.

The c/a ratio for doped materials are significantly lower compared to pure lead titanate. The lower c/a ratio is a desirable feature as the materials showing less tetragonality are less susceptible to thermal shock. The explanation for this is that large differences in lattice dimensions result in large differences between the rates of thermal expansion along different axes. These differences set up mechanical stresses that result in macro or micro cracking of the ceramic body while cooling through the Curie temperature. The large anisotropy in the crystal structure is the reason why pure $PbTiO_3$ will not sinter and must be doped in order to obtain a useable product. Lowering of unit cell tetragonality has also previously been reported (8-14) for other doped lead titanates.

Scanning electron micrographs (SEM)

SEM yielded valuable information on the microstructure of the sintered bodies. Both the polished sections and fractured surface samples were used for SEM studies.

SEM of fractured surfaces involved the imaging of a surface exposed by deliberately breaking the sample. The exposed surfaces showed intergranular fracturing between crystalline grains (Fig. 2a and 2b). These figures also show the difference between pellets

made from powders that were not attrition milled after calcination (Fig. 2a) and those that were (Fig. 2b). Attrition milling not only reduces particle size, but also results in a more uniform particle size distribution (2-4 micron grains after versus 4-10 microns before re-attrition milling). The large tetragonal grains visible in Fig.2A form during calcination and hinder close packing of the grains. The resulting porosity causes low measured densities.

Polished section specimens for SEM were prepared by grinding down and polishing a fragment of a pellet to reveal an internal section of the pellet. This method yielded little useful information, except in the case of D2 (Fig.3a). These micrographs reveal a 3-phase material. Elemental analysis showed a sodium deficient $PbTiO_3$ type matrix (atomic ratio Na:Pb:Ti=1:9:8.24) and two types of sodium-rich, lead-deficient inclusions (Na:Pb:Ti=10.9:1:26.1 and 4.9:1:22.4). Figures 3b,c and d show the distribution of lead (Pb L-Alpha line), titanium (Ti K-Alpha) and sodium (Na K-Alpha) respectively for the same sample as determined by an SEM microprobe. Such multi-phased materials are unsuited to application as high frequency ultrasonic transducers.

CONCLUSIONS

Compared to pure lead titanate, modified lead titanates having alkaline-earth and rare-earth oxides as major dopants exhibit lower crystal tetragonality (c/a ratio ref. Table 2). Similar results have been previously reported for other modified lead titanate compositions(9-14). The data in Table 2 also suggests that with the exception of D2, these materials can be sintered to high densities (~95% or higher). The high soda content appears to promote the low densification in D2. SEM micrographs and EDX analysis have revealed soda rich, lead deficient inclusions that

may be responsible for the observed low density of this material. Further microstructural studies are needed to explain this behavior. Although sample D4, having the lowest c/a value of 1.028 exhibited the highest density, no direct correlation between the sample density and unit cell tetragonality can be arrived at from Table 2.

The surface areas of the powders show dependence on the powder composition, calcination temperature, re-attrition milling and the powder drying method. Cerium doped powders produced by filtration and oven drying yield materials with the highest surface area. This high surface area (smaller particle size) may be the reason for observed high density (>97%) in this material after sintering.

Calcination of the powders causes partial sintering of the material giving relatively large agglomerated particles having low surface areas. These large agglomerates hinder close packing of the particles resulting in reduced high temperature densification of the material. This problem can be solved by re-attrition milling. SEM studies show that re-attrition milling of the calcined powders furnish smaller particle size and more uniform particle size distribution resulting in relatively lower porosity or improved sintered densities.

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Table 1. Surface areas of powders made by various methods

POWDER TYPE	DRYING METHOD	SURFACE AREA (m^2/g)		
		Before Calcining	After Calcining	After Regrinding
D1	spray-dried	6.78	1.38	4.11
D2	spray-dried	5.08	1.08	4.45
D3	rotary evap.	4.21	0.92	4.30
D4	filtered oven-dried	10.70	1.90	8.98

Table 2. Tetragonality and density of various samples

Powder	c/a	Theoretical Density (g/cc)	% theor. Density (g/cc)	Sintering Temp. (°C)
D1	1.042	7.269	95.20	1175
D2	1.039	7.686	92.17	950
D3	1.045	7.955	94.80	1050
D4	1.028	7.492	96.50	1050
$PbTiO_3$	1.065	7.971	-	-

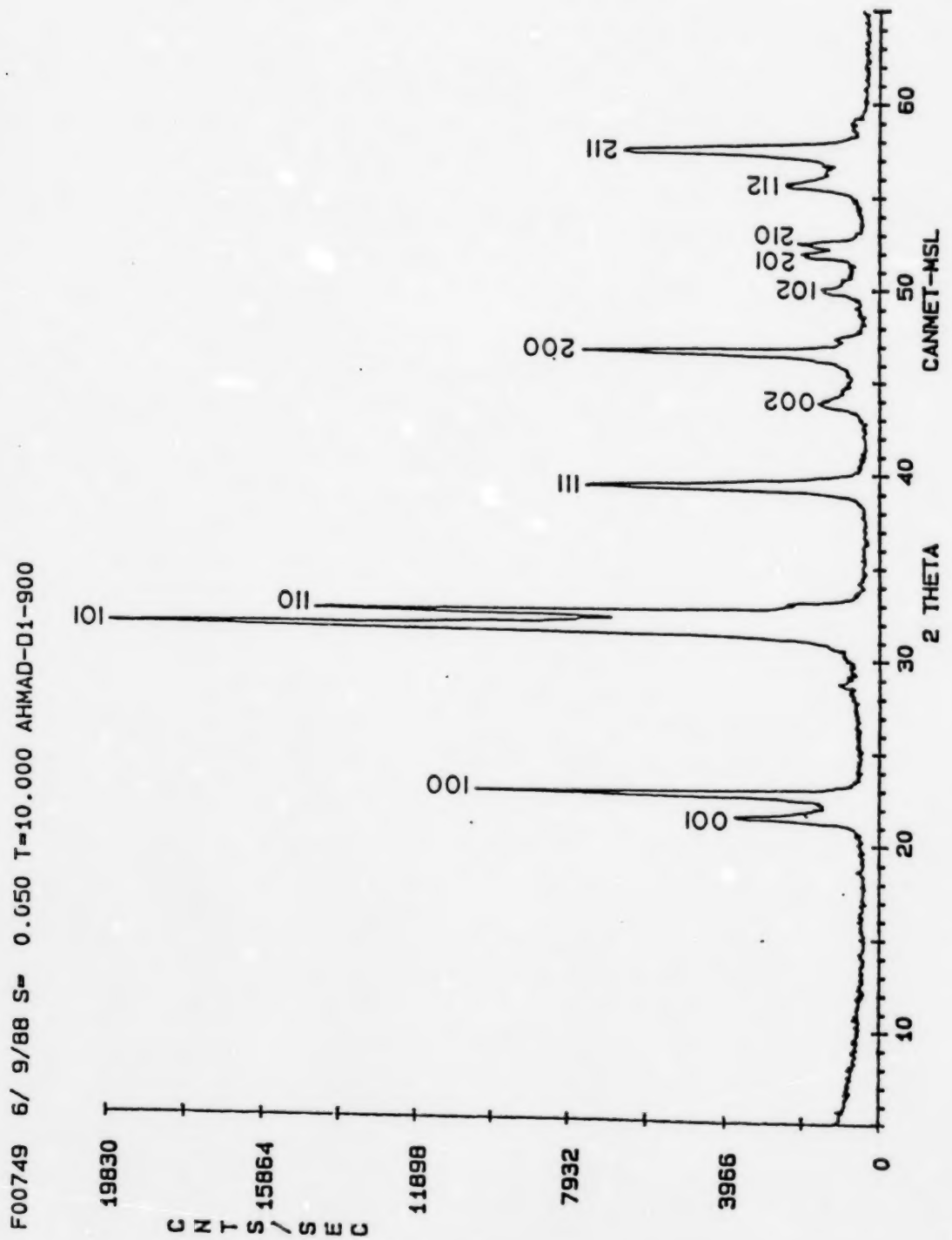
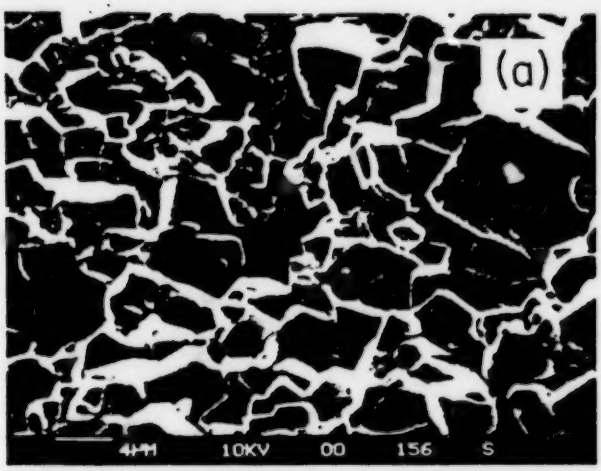


Fig. 1 XRD pattern of D1 powder calcined at 900 deg. C.



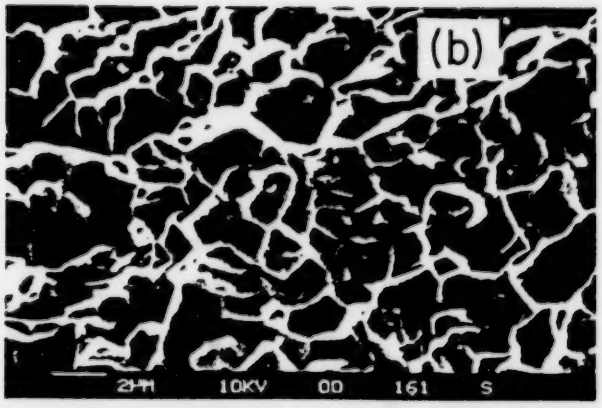


Fig. 2 - SEM micrographs of fractured samples (D1)
(a) sintered using as calcined powders and
(b) sintered using re-attrition milled calcined powders.

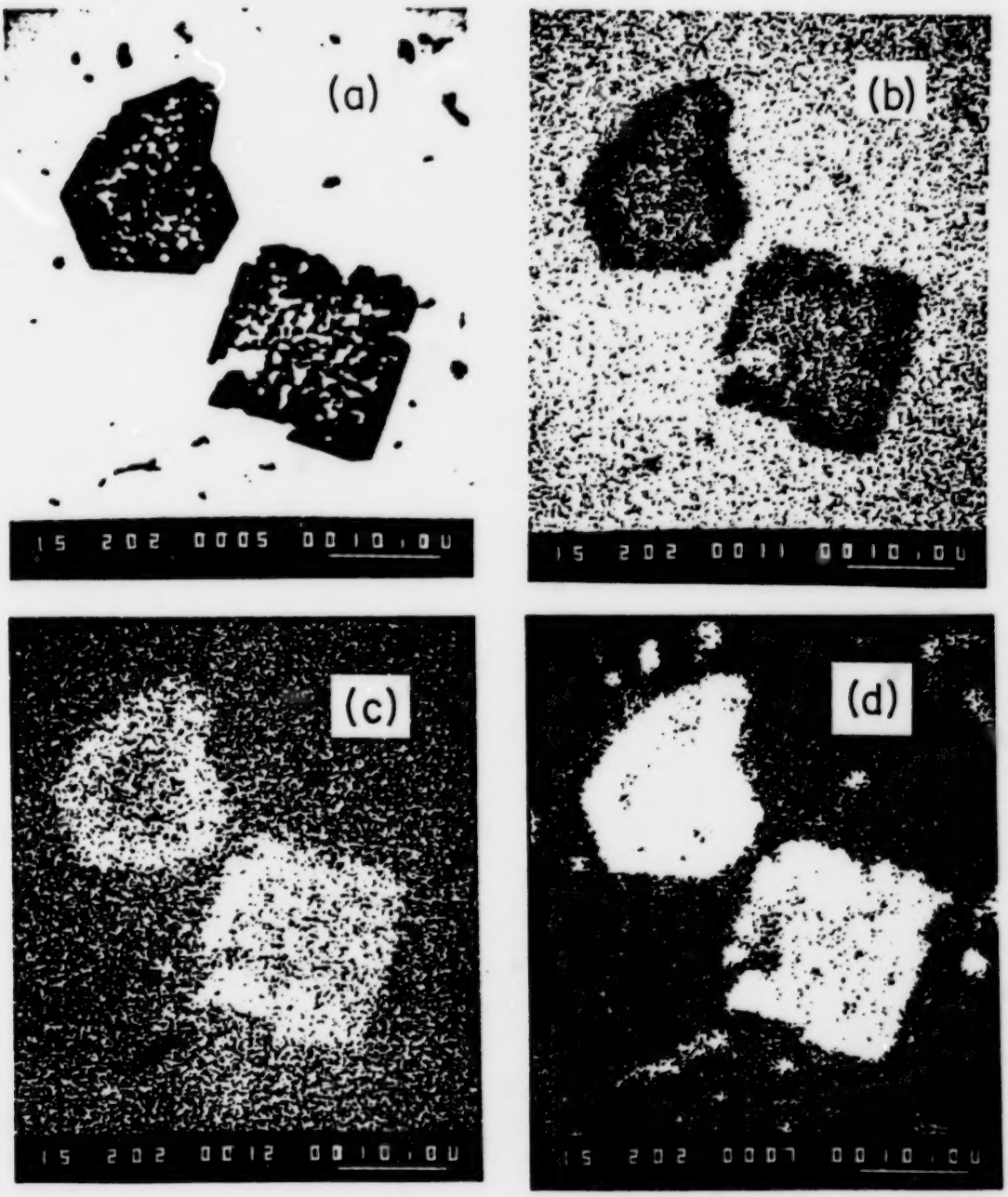


Fig. 3 - (a) SEM micrograph of polished section of D2 showing inclusions. (b) Microprobe scan of D2 revealing lead distribution. (c) Titanium distribution in D2. (d) Sodium distribution in D2. Light areas are high in elemental distribution, dark areas are low in elemental distribution.